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(54) Title: PREMOISTENED WIPE WITH RESIDUAL ANTIMICROBIAL ACTIVITY (57) Abstract A method of obtaining effective residual antimicrobial activity on a hard surface comprises contacting a hard surface with an effective amount of an antimicrobial composition comprising an organic acid and surfactant and allowing specific amounts of the organic acid and surfactant to remain on the treated hard surface. A premoistened wipe of the present invention comprises an antimicrobial composition and a substrate. An article of manufacture of the present invention comprises a container, premoistened wipes, and a set of instructions.		

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PREMOISTENED WIPE WITH RESIDUAL ANTIMICROBIAL ACTIVITY

TECHNICAL FIELD

The present invention relates to a method of obtaining effective residual antimicrobial activity on a hard surface and premoistened wipes therefor. In particular, the method of the present invention comprises contacting a hard surface with an antimicrobial composition comprising an organic acid and surfactant and allowing specific amounts of the organic acid and surfactant to remain on the hard surface. The premoistened wipes of the present invention comprise an antimicrobial composition and a substrate.

BACKGROUND OF THE INVENTION

Hard surfaces found in the household, such as countertops in kitchens and bathrooms, are often contaminated with bacteria and other microorganisms. These microorganisms can lead to illnesses in humans and in animals. Humans are especially vulnerable to these microorganisms when they are present near food, such as on the countertops in kitchens and dining rooms.

The antimicrobial effectiveness of organic acids, such as citric acid, is well known throughout the literature. Organic acids are utilized in a few cleaning products to provide antimicrobial effectiveness. However, most antimicrobial cleaning products provide only immediate antimicrobial activity and do not provide residual antimicrobial activity. For example, most antimicrobial spray cleaning products are sprayed onto a surface to provide immediate antimicrobial activity and then rinsed, wiped, or otherwise removed from the surface treated. Many of these products would not be safe to leave on a surface, especially on surfaces around food, such as kitchen countertops. Other antimicrobial products are simply not efficacious over a period of time to provide residual antimicrobial effectiveness.

There has thus been a need for a safe antimicrobial product that provides residual antimicrobial activity. There has also been a need for a way to treat hard surfaces, such as countertops in kitchens and bathrooms, so that surfaces free of microorganisms will not be recontaminated by other microorganisms.

SUMMARY OF THE INVENTION

The present invention relates to a method of obtaining effective residual antimicrobial activity on a hard surface comprising the steps of:

- (a) contacting said hard surface with an effective amount of an antimicrobial composition comprising organic acid having antimicrobial action, preferably citric acid, and surfactant, preferably a nonionic surfactant; and
- (b) allowing at least about 100 micrograms (μg), preferably at least about 150 μg , more preferably at least about 175 μg , and still more preferably at least about 275 μg , of the organic acid and at least about 100 μg , preferably at least about 125 μg , more preferably at least about 150 μg , and still more preferably at least about 175 μg , of the surfactant per square inch of said hard surface to remain on said hard surface.

The method of the present invention provides a residual antimicrobial benefit on the treated surface for an indefinite period of time, so long as the specific levels of organic acid and surfactant are allowed to remain on the treated surface. The method provides residual antimicrobial effectiveness against a variety of microbes, including *Salmonella choleraesuis* and *Staphylococcus aureus*.

The present invention further relates to a premoistened wipe comprising:

- (a) substrate; and
- (b) antimicrobial composition comprising:
 - (i) antimicrobially effective amount of organic acid;
 - (ii) surface tension reducing amount of surfactant;
 - (iii) optionally, suds suppressor;
 - (iv) optionally, hydrotrope;
 - (v) optionally, solvent;
 - (vi) optionally, perfume; and
 - (vii) water.

The antimicrobial composition typically has a pH of from about 1.6 to about 3.0 and is typically loaded onto the substrate at a loading factor of at least about 2.0. The premoistened wipe of the present invention can be utilized to carry out the method of the present invention to obtain effective residual antimicrobial activity.

The present invention also relates to articles of manufacture for obtaining effective residual antimicrobial activity on a hard surface comprising (a) a container, (b) premoistened wipes comprising antimicrobial composition, and (c) set of instructions to apply said antimicrobial

composition to a hard surface and allow an effective residual antimicrobial activity amount of said antimicrobial composition on said hard surface to obtain effective residual antimicrobial activity on said surface.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the phrase "effective residual antimicrobial activity" means that at least a one log reduction, preferably at least a two log reduction, and more preferably at least a three log reduction in microbial activity is achieved when a hard surface, which has been treated according to the method of the present invention, is inoculated with about 10 microliters of inoculum comprising from about 10^4 to about 10^7 microorganism count. A test method for determining effective residual antimicrobial activity on a surface treated with an antimicrobial composition of the present invention is described hereinafter in Example I.

As used herein, the term "effective amount" means an amount of an antimicrobial composition that provides the necessary amounts of organic acid and surfactant to the treated surface to achieve effective residual antimicrobial activity.

The present invention encompasses methods of obtaining effective residual antimicrobial activity on a hard surface. Also encompassed by the present invention are antimicrobial compositions and premoistened wipes comprising antimicrobial composition and substrate for carrying out the method of the present invention. Also, the present invention includes articles of manufacture comprising (a) container, (b) premoistened wipes comprising antimicrobial composition, and (c) set of instructions to apply said antimicrobial composition to a hard surface and allow an effective residual antimicrobial activity amount of said antimicrobial composition on said hard surface to obtain effective residual antimicrobial activity on said surface. The methods, premoistened wipes, and articles of the present invention are effective against a variety of microbes, including gram negative (-) and gram positive (+) bacteria.

METHOD OF OBTAINING EFFECTIVE RESIDUAL ANTIMICROBIAL ACTIVITY

The present invention encompasses methods of achieving effective residual antimicrobial activity on a hard surface by contacting the surface with an effective amount of an antimicrobial composition comprising organic acid having antimicrobial action and an effective amount to reduce surface tension of surfactant, and allowing specific amounts of the organic acid and surfactant to remain on the treated hard surface. In typical hard surfaces cleaning methods, the cleaning compositions are rinsed from the surface after being applied. An important aspect of the present methods is that specific amounts of organic acid and surfactant are allowed to remain on the treated surface. When the treated surface is subsequently inoculated with about 10 microliters

of bacteria, at least a one log reduction in microbial activity is exhibited. This residual antimicrobial activity results for an indefinite period of time, including periods of time such as 18 hours or even 24 hours, so long as the specific amounts of organic acid and surfactant are allowed to remain on the treated surface.

To achieve at least a residual one log reduction in microbial activity on a hard surface, the hard surface is contacted with an effective amount of an antimicrobial composition of the present invention and at least about 100 μg , preferably at least about 150 μg , more preferably at least about 175 μg , and still more preferably at least about 275 μg , of organic acid and at least about 100 μg , preferably at least about 125 μg , more preferably at least about 150 μg , and still more preferably at least about 175 μg of surfactant, per square inch of the treated hard surface are allowed to remain on the treated surface. The specific amounts required for any specific organic acid having antimicrobial action and/or surfactant can be readily determined using the test method disclosed hereinafter in Example I.

In a preferred embodiment, the organic acid is citric acid and the surfactant is a nonionic surfactant, preferably an ethoxylated alcohol (such as ALFONIC® 810-6 Ethoxylated available from Vista Chemical Company in Houston, Texas) as described hereinafter. Allowing a combination of specific amounts of citric acid and nonionic surfactant to remain on a hard surface surprisingly provide effective residual antimicrobial activity on the hard surface, which protects the surface against recontamination by a variety of microbes, including gram negative (-) bacteria, such as *Salmonella choleraesuis*, and gram positive (+) bacteria, such as *Staphylococcus aureus*. In addition, the combination of citric acid and nonionic surfactant can provide a glossy or shiny film on the treated surface which can be both aesthetically appealing to consumers and provide a visual signal to consumers that the surface has residual antimicrobial protection. Also, the glossy film allows the consumer to identify areas on the hard surface which were inadvertently missed in treating the surface and allows the consumer to verify that an entire area has been treated.

The hard surface to be treated can be contacted by the antimicrobial composition in a variety of ways in the method of the present invention. For example, the antimicrobial composition can be sprayed directly onto the surface using conventional sprayers known in the art; sprayed onto a substrate, such as a paper towel, typically to the point of saturation, and then wiping the surface with the substrate; wiping the surface with a premoistened wipe comprising an antimicrobial composition and a substrate, such as those of the present invention described hereinafter; and other similar methods of contacting the surface to be treated.

PREMOISTENED WIPE

The premoistened wipe of the present invention typically comprises an antimicrobial composition and a substrate. The methods of the present invention can be carried out by applying the specific amounts of organic acid and surfactant to a hard surface to be treated by wiping the surface with the premoistened wipes of the present invention.

(A) ANTIMICROBIAL COMPOSITION

The present invention encompasses antimicrobial compositions typically comprising an organic acid having antimicrobial action, preferably citric acid, and surfactant, preferably nonionic surfactant. The antimicrobial compositions can further comprise optional ingredients such as suds suppressors, hydrotropes, solvents, perfume, hydrogen peroxide, chelating agents, radical scavengers, and other optional ingredients. The methods of the present invention can be carried out using the antimicrobial composition itself, or by loading the antimicrobial composition onto a substrate form a premoistened wipe and using the premoistened wipe to carry out the present methods.

(i) ANTIMICROBIAL ORGANIC ACID

The present invention results from the unexpected discovery that certain organic acids such as citric, malic, succinic, and benzoic, used in suitable concentrations, as further described herein, are highly efficacious against microbes, such as *Salmonella choleraesuis* and *Staphylococcus aureus*. When used in the presence of a surfactant, preferably a nonionic surfactant such as alcohol ethoxylates (for example, ALFONIC® 810-6 Ethoxylated available from Vista Chemical Company in Houston, Texas), these acids were found to have effective residual antimicrobial activity against a variety of microbes, including gram negative (-) bacteria, such as *Salmonella choleraesuis*, and gram positive (+) bacteria, such as *Staphylococcus aureus*. In general, the water soluble carboxylic acids useful in accordance with the invention have the following structure:



wherein R may be represented by: lower alkyl; substituted lower alkyl; hydroxy lower alkyl (e.g. HOCH_2-); carboxy lower alkyl (e.g. $\text{HOOC-CH}_2\text{-CH}_2-$); carboxy, hydroxy lower alkyl (e.g., $\text{HOOCCH}_2\text{CHOH-}$); carboxy, halo lower alkyl (e.g. $\text{HOOCCH}_2\text{CHBr-}$); carboxy, dihydroxy lower alkyl (e.g. HOOC-CHOH-CHOH-); dicarboxy, hydroxy lower alkyl (e.g. $\text{HOOC-CH}_2\text{-C(OH)(COOH)H}_2-$); lower alkenyl, carboxy lower alkenyl (e.g. HOOCCH=CH-); dicarboxy lower alkenyl (e.g. $\text{HOOC-CH}_2\text{C(COOH)=CH-}$); phenyl (C_6H_5-); substituted phenyl (e.g. hydroxy phenyl $\text{HO-C}_6\text{H}_4-$). Other acid examples include hydroxy lower alkyl e.g. lactic; carboxy, hydroxy lower alkyl, e.g. 2-methyl malic; carboxy, halo lower alkyl, e.g. 2-chloro-3-

methyl succinic; carboxy, dihydroxy lower alkyl, e.g. 2-methyl tartaric; dicarboxy, hydroxy lower alkyl, e.g. 2-methyl citric acid; and carboxy lower alkenyl, e.g. fumaric. The above definitions are used in an illustrative but not a limiting sense. The term "lower" as used herein refers to an acid wherein "R" contains one to six carbon atoms. The term "substituted" indicates that one or more hydrogen atoms are substituted by halogen atoms (F, Cl, Br, I) hydroxyl groups, amino groups, thiol groups, nitro groups, cyano groups, and the like. Examples of preferred antimicrobial organic acids include, but are not limited to, citric acid, lactic acid, malic acid, salicylic acid, acetic acid, and mixtures thereof.

In a preferred embodiment, the present antimicrobial compositions comprise organic acid at a level of from about 0.5% to about 20%, more preferably from about 1% to about 10%, and still more preferably from about 1.5% to about 7.5% by weight of the antimicrobial composition. Citric acid is a highly preferred organic acid having antimicrobial action. Citric acid is preferred because it is a natural acid and is relatively safe for use on household surfaces, especially surfaces used for food preparation such as countertops in kitchens and dining rooms. In addition, when citric acid is allowed to remain on a surface, it tends to provide a glossy or shiny film on the surface which can be aesthetically satisfying to consumers and provide a visual signal to consumers that the surface has residual antimicrobial protection. Also, the glossy film allows the consumer to identify areas on the hard surface which were inadvertently missed in treating the surface and allows the consumer to verify that an entire area has been treated.

(ii) SURFACTANT

It is believed that surfactant is needed to aid the antimicrobial action of the organic acid, especially when the organic acid is present in relatively small amount, by functioning to disrupt the cell walls of the microbes to allow the organic acid to easily penetrate into the cell body, thereby inactivating the microbe. Suitable surfactants for incorporation in the present antimicrobial compositions include those known in the art selected from nonionic, anionic, zwitterionic, ampholytic, cationic surfactants, and mixtures thereof. Preferably, the surfactant utilized in the present antimicrobial compositions is a nonionic surfactant, more preferably an ethoxylated nonionic surfactant. Typically, the present antimicrobial compositions comprise from about 0.5% to about 15%, preferably from about 1% to about 10%, more preferably from about 1.5% to about 5%, of surfactant by weight of the antimicrobial composition.

Most preferably, the present antimicrobial compositions comprise ethoxylated nonionic surfactants, which can be broadly defined as compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be

aliphatic or alkyl aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. In general, ethoxylated nonionic surfactants suitable herein have an average ethyleneoxy content in the range from about 35% to about 70%, by weight of the surfactant.

Examples of suitable nonionic surfactants include the condensation products of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms in either straight chain or branched chain configuration with from 2 to about 18 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8, moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty and greasy soils. The preferred surfactants are prepared from primary alcohols having no more than about 50% chain branching, i.e., which are either linear (such as those derived from natural fats or prepared by the Ziegler process for ethylene, e.g., myristyl, cetyl, stearyl alcohols) or partly branched such as the DOBANOLs and NEODOLs, which have about 25% 2-methyl branching (DOBANOLTM and NEODOL[®] being trade names of Shell Oil Company) or SYNPERONICs, which are understood to have about 40% to 50% 2-methyl branching. (SYNPERONIC[®] is a trade name of Imperial Chemical Industries PLC) Specific examples of nonionic surfactants falling within the scope of the invention include DOBANOLTM 45-4, DOBANOLTM 45-7, DOBANOLTM 45-9, DOBANOLTM 91-3, DOBANOLTM 91-6, DOBANOLTM 91-8, SYNPERONIC[®] 6, SYNPERONIC[®] 9, the condensation products of coconut alcohol with an average of between 5 and 9 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, for example, those ethoxylates of the Tergitol series having from about 9 to 15 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

Of the above, highly preferred are alkoxyated nonionic surfactants having an average HLB in the range from about 9.5 to 13.5, especially 10 to 12.5. Highly suitable nonionic surfactants of this type are ethoxylated primary C₈₋₁₅ alcohols having an average degree of ethoxylation from about 2 to 9, more preferably from about 3 to 8. Most preferably, the surfactant is an ethoxylated C₈₋₁₀ alcohol having an average degree of ethoxylation of about 6, which is

commercially available from Vista Chemical Company in Houston, Texas under the trade name ALFONIC® 810-6 Ethoxylated. Other useful nonionic surfactants include carbohydrate based surfactants and amine oxides based on olefins.

Alternatively, or in addition to nonionic surfactants, other surfactants can be utilized in the antimicrobial compositions including anionic, amphoteric, zwitterionic, and cationic surfactants.

Suitable anionic surfactants to be used herein include water soluble salts or acids of the formula ROSO_3M wherein R is preferably a $\text{C}_6\text{-C}_{24}$ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a $\text{C}_{10}\text{-C}_{20}$ alkyl component, more preferably a $\text{C}_{12}\text{-C}_{18}$ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Other suitable anionic surfactants to be used herein include alkyl-diphenyl-ether-sulphonates and alkyl-carboxylates. Other anionic surfactants can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, $\text{C}_9\text{-C}_{20}$ linear alkylbenzenesulfonates, $\text{C}_8\text{-C}_{22}$ primary or secondary alkanesulfonates, $\text{C}_8\text{-C}_{24}$ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, $\text{C}_8\text{-C}_{24}$ alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as $\text{C}_{14}\text{-C}_{16}$ methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated $\text{C}_{12}\text{-C}_{18}$ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated $\text{C}_6\text{-C}_{14}$ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_k\text{CH}_2\text{COO-M}^+$ wherein R is a $\text{C}_8\text{-C}_{22}$ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived

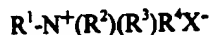
from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Preferred anionic surfactants for use in the compositions herein are the alkyl benzene sulfonates, alkyl sulfates, alkyl alkoxyated sulfates, paraffin sulfonates and mixtures thereof.

Suitable amphoteric surfactants to be used herein include amine oxides having the following formula $R^1R^2R^3NO$ wherein each of R^1 , R^2 and R^3 is independently a saturated substituted or unsubstituted, linear or branched hydrocarbon chains of from 1 to 30 carbon atoms. Preferred amine oxide surfactants to be used according to the present invention are amine oxides having the following formula $R^1R^2R^3NO$ wherein R^1 is an hydrocarbon chain comprising from 1 to 30 carbon atoms, preferably from 6 to 20, more preferably from 8 to 16, most preferably from 8 to 12, and wherein R^2 and R^3 are independently substituted or unsubstituted, linear or branched hydrocarbon chains comprising from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups. R^1 may be a saturated substituted or unsubstituted, linear or branched hydrocarbon chain.

Suitable amine oxides for use herein are for instance natural blend C_8 - C_{10} amine oxides as well as C_{12} - C_{16} amine oxides commercially available from Hoechst.

Suitable zwitterionic surfactants to be used herein contain both cationic and anionic hydrophilic groups on the same molecule at a relatively wide range of pH's. The typical cationic group is a quaternary ammonium group, although other positively charged groups like phosphonium, imidazolium and sulfonium groups can be used. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphonates, and the like can be used. A generic formula for some zwitterionic surfactants to be used herein is



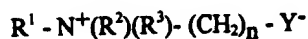
wherein R^1 is a hydrophobic group; R^2 and R^3 are each C_1 - C_4 alkyl, hydroxy alkyl or other substituted alkyl group which can also be joined to form ring structures with the N; R^4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 10 carbon atoms; and X is the hydrophilic group which is preferably a carboxylate or sulfonate group. Preferred hydrophobic groups R^1 are alkyl groups containing from 1 to 24, preferably less than 18, more preferably less than 16 carbon atoms. The hydrophobic group can contain unsaturation and/or substituents and/or linking groups

such as aryl groups, amido groups, ester groups and the like. In general, the simple alkyl groups are preferred for cost and stability reasons.

Highly preferred zwitterionic surfactants include betaine and sulphobetaine surfactants, derivatives thereof or mixtures thereof. Said betaine or sulphobetaine surfactants are preferred herein as, they help disinfection by increasing the permeability of the bacterial cell wall, thus allowing other active ingredients to enter the cell.

Furthermore, due to the mild action profile of said betaine or sulphobetaine surfactants, they are particularly suitable for the cleaning of delicate surfaces, e.g., surfaces in contact with food and/or babies. Betaine and sulphobetaine surfactants are also extremely mild to the skin and/or surfaces to be treated.

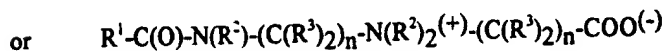
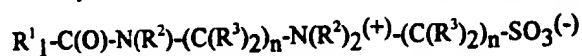
Suitable betaine and sulphobetaine surfactants to be used herein are the betaine/sulphobetaine and betaine-like detergents wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of pH values. Some common examples of these detergents are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference. Preferred betaine and sulphobetaine surfactants herein are according to the formula:



wherein R^1 is a hydrocarbon chain containing from 1 to 24 carbon atoms, preferably from 8 to 18, more preferably from 12 to 14, wherein R^2 and R^3 are hydrocarbon chains containing from 1 to 3 carbon atoms, preferably 1 carbon atom, wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably is 1, Y is selected from the group consisting of carboxyl and sulfonyl radicals and wherein the sum of R^1 , R^2 and R^3 hydrocarbon chains is from 14 to 24 carbon atoms, or mixtures thereof.

Examples of particularly suitable betaine surfactants include C_{12} - C_{18} alkyl dimethyl betaine such as coconut-betaine and C_{10} - C_{16} alkyl dimethyl betaine such as laurylbetaine. Coconutbetaine is commercially available from Seppic under the trade name of Amonyl 265®. Laurylbetaine is commercially available from Albright & Wilson under the trade name Empigen BB/L®.

Other specific zwitterionic surfactants have the generic formulas:



wherein each R^1 is a hydrocarbon, e.g. an alkyl group containing from 8 up to 20, preferably up to 18, more preferably up to 16 carbon atoms, each R^2 is either a hydrogen (when attached to the amido nitrogen), short chain alkyl or substituted alkyl containing from one to 4 carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl, each R^3 is selected from the group consisting of hydrogen and hydroxy groups and each n is a number from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R^3)_2)_n$ moiety. The R^1 groups can be branched and/or unsaturated. The R^2 groups can also be connected to form ring structures. A surfactant of this type is a C_{10} - C_{14} fatty acylamidopropylene(hydroxypropylene)sulfobetaine that is available from the Sherex Company under the trade name "Varion CAS sulfobetaine"®.

Suitable cationic surfactants that can be used in the detergent compositions of the present invention include coconut trimethylammonium chloride.

(iii) SUDS SUPPRESSOR

Optionally, but preferably, the present antimicrobial composition comprises a suds suppressor to limit the amount of suds generated when the antimicrobial composition is applied to a hard surface. An important aspect of the present invention involves allowing the antimicrobial composition to remain on the treated surface, without being rinsed off or otherwise significantly removed. As such, it can be important to provide an antimicrobial composition that minimizes visual residue so as to be consumer acceptable. Suds suppressors can be incorporated in the antimicrobial compositions of the present invention to reduce the amount of visual residue remaining on the treated surface. Suds tend to leave an unappealing visual residue on the treated surface which can be unacceptable to consumers of the present article of manufacture. This can especially be a problem when the antimicrobial compositions are not rinsed and/or wiped from the treated surface, as in the present methods for achieving effective residual antimicrobial activity.

Suds suppressors useful in the antimicrobial compositions of the present invention include alkyl phosphate ester suds suppressors, silicone suds suppressors, and combinations thereof. Levels in general are from 0% to about 10%, preferably from about 0.001% to about 5%, and more preferably from about 0.003% to about 1%, by weight of the antimicrobial composition. Typical levels tend to be low, e.g., from about 0.01% to about 3% when a silicone suds suppressor is used. Preferred non-phosphate compositions omit the phosphate ester component entirely. Silicone suds suppressor technology and other defoaming agents useful herein are more extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P. R. Garrett, Marcel

Dekker, N.Y., 1973, ISBN 0-8247-8770-6, incorporated herein by reference. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Pat. Nos. 3,933,672 and 4,136,045. Other useful suds suppressors can be found in U.S. Patent No. 5,500,154. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxanes having trimethylsilyl or alternate end blocking units may be used as the silicone. These may be compounded with silica and/or with surface-active non-silicon components, as illustrated by a suds suppressor comprising 12% silicone/silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp. A highly preferred suds suppressor is a silicone compound available from Dow Corning Corp. under the trade name DOW AF™. Phosphate esters have also been asserted to provide some protection of silver and silver-plated utensil surfaces; however, the instant compositions can have excellent silver care without a phosphate ester component. If it is desired nonetheless to use a phosphate ester, suitable compounds are disclosed in U.S. Pat. No. 3,314,891, issued Apr. 18, 1967, to Schmolka et al, incorporated herein by reference. Preferred alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are monostearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof. It has been found preferable to avoid the use of simple calcium-precipitating soaps as antifoams in the present compositions as they tend to deposit on the dishware. Indeed, phosphate esters are not entirely free of such problems and the formulator will generally choose to minimize the content of potentially depositing antifoams in the instant compositions.

(iv) HYDROTROPE

An optional ingredient which is sometimes highly desirable in aqueous liquid cleaners is a hydrotrope which serves to stabilize the compositions by aiding in the solubilization of their components. A hydrotrope is especially preferred for use in an antimicrobial composition which also comprises perfume materials, solvents, and multiple surfactant systems. In such an antimicrobial composition, the hydrotrope serves to solubilize the otherwise insoluble materials. The hydrotrope is typically selected from the group consisting of alkali metal, ammonium, and triethanolammonium isopropylbenzene sulfonates, xylene sulfonates, toluene sulfonates, cumene sulfonates, benzene sulfonates, and mixtures thereof. Specific hydrotropes found to be useful in the present antimicrobial compositions are sodium cumene sulfonate and potassium toluene

sulfonate. Most preferably, sodium cumene sulfonate is incorporated in the present antimicrobial compositions. When present, hydrotropes are incorporated in the antimicrobial compositions at a level from about 0% to about 5%, preferably from about 1% to about 3%, more preferably from about 1.2% to about 2% by weight of the antimicrobial composition. The hydrotrope, e.g. sodium cumene sulfonate, serves only to stabilize the antimicrobial compositions by aiding the solubilization of the various ingredients.

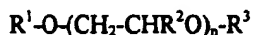
(v) SOLVENT

The compositions herein may comprise as an optional ingredient a solvent or mixtures thereof. When used, solvents will, advantageously, give an enhanced cleaning to the compositions of the present invention. Suitable solvents for incorporation in the compositions according to the present invention include propylene glycol derivatives such as n-butoxypropanol or n-butoxypropoxypropanol, water-soluble CARBITOL® solvents or water-soluble CELLOSOLVE® solvents. Water-soluble CARBITOL® solvents are compounds of the 2-(2-alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl or butyl. A preferred water-soluble carbitol is 2-(2-butoxyethoxy)ethanol also known as butyl carbitol. Water-soluble CELLOSOLVE® solvents are compounds of the 2-alkoxyethoxyethanol class, with 2-butoxyethoxyethanol being preferred. Other suitable solvents are benzyl alcohol, methanol, ethanol, isopropyl alcohol and diols such as 2-ethyl-1,3-hexanediol and 2,2,4-trimethyl-1,3-pentanediol and mixture thereof. Preferred solvents for use herein are n-butoxypropoxypropanol, butyl carbitol® and mixtures thereof. Most preferably, the solvent for use in the present antimicrobial compositions is n-butoxypropoxypropanol (also referred to as dipropylene glycol monobutyl ether). N-butoxypropoxypropanol is typically utilized in the present antimicrobial compositions at a level of from about 0% to about 6%, preferably from about 0.5% to about 4%, more preferably from about 0.5% to about 1.5% by weight of the antimicrobial composition.

Other useful solvents for use in the present antimicrobial compositions include a poly(alkylene glycol) alkyl ether, as defined herein after, or mixtures thereof.

Typically, where present the composition may comprise a poly(alkylene glycol) alkyl ether or a mixture thereof at a level of from 0.001% to 10%, preferably from 0.005% to 2%, more preferably from 0.01% to 1%, even more preferably from 0.05% to 0.5% and most preferably from 0.08% to 0.4% by weight of the total composition.

Suitable poly(alkylene glycol) alkyl ethers for use herein are according the following formula:



wherein R^1 and R^2 each independently are hydrogen or a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 1 to 30 carbon atoms or a hydroxy bearing linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, R^3 is a substituted or unsubstituted, saturated or unsaturated, linear or branched hydrocarbon chain having from 1 to 30 carbon atoms or a hydroxy bearing linear or branched hydrocarbon chain having from 1 to 30 carbon atoms, n is a number greater than 2, or a mixture thereof.

Preferably R^1 and R^2 each independently are hydrogen, or a substituted or unsubstituted, linear or branched, alkyl group or alkenyl group having from 1 to 30 carbon atoms, preferably from 1 to 16 carbon atoms, more preferably from 1 to 8 and most preferably from 1 to 4, or a hydroxy bearing linear or branched alkyl or alkenyl group having from 1 to 30 carbon atoms, more preferably from 1 to 16, even more preferably from 1 to 4, and most preferably R^1 and R^2 are methyl or hydrogen.

Preferably R^3 is a substituted or unsubstituted, linear or branched, alkyl group or alkenyl group having from 1 to 30 carbon atoms, preferably from 1 to 16 carbon atoms, more preferably from 1 to 8 and most preferably from 1 to 4, or a substituted or unsubstituted, saturated or unsaturated, linear or branched aryl group having up to 30 carbon atoms, preferably from 3 to 16 and more preferably from 4 to 8 carbon atoms, or a hydroxy bearing linear or branched alkyl or alkenyl group having from 1 to 30 carbon atoms, more preferably from 1 to 16 even more preferably from 1 to 8, and most preferably R^3 is butyl.

Preferably n is a number of at least 3, preferably from 3 to 2300, more preferably 3 to 100, more preferably from 3 to 20 and most preferably from 3 to 10.

The poly(alkylene glycol) alkyl ethers for use herein preferably have an average molecular weight from 164 to 100,000, more preferably from 180 to 10,000 and most preferably from 200 to 1,000.

Suitable poly(alkylene glycol) alkyl ethers for use herein include poly(propylene glycol) mono butyl ether, poly(ethylene glycol-co-propylene glycol) mono butyl ether, poly(ethylene glycol) dimethyl ether, poly(ethylene glycol-co-propylene glycol) dimethyl ether, poly(ethylene glycol) stearate or mixtures thereof. Poly(propylene glycol) mono butyl ether (average molecular weight 340) is commercially available from Aldrich or from Union Carbide under Ucon-1b 65®.

Other useful solvents for antimicrobial compositions of the present invention include those disclosed in U.S. Patent Nos. 5,540,865; 5,435,935; and 5,362,422; which are hereby incorporated by reference.

The solvents may typically be present within the compositions of the invention at a level up to 15% by weight, and preferably from 1% to 7% by weight of the composition.

(vi) PERFUME

Perfumes are optionally, but preferably, incorporated in the present antimicrobial compositions to impart an aesthetically satisfying odor to the antimicrobial composition. A variety of perfume materials can be utilized, especially those imparting odor characters such as citrus, pine, and outdoor fresh. If perfume materials are utilized in the present antimicrobial compositions, a hydrotrope, such as sodium cumene sulfonate as described hereinbefore, is typically needed in order to solubilize the perfume materials and stabilize the antimicrobial composition.

(vii) OTHER OPTIONAL INGREDIENTS

Other optional ingredients such as chelating agents, radical scavengers, and dyes can be incorporated into the present antimicrobial compositions. Peroxygen bleach, such as hydrogen peroxide, is another optional ingredient that can be utilized in the antimicrobial compositions to improve the antimicrobial activity of the antimicrobial compositions. However, because peroxygen bleach tends to be rather unstable, the present antimicrobial compositions are essentially free of peroxygen bleach, such as hydrogen peroxide.

The balance of the formula is typically water and/or non-aqueous polar solvents with only minimal cleaning action, e.g., those having a hydrogen bonding parameter above 7.8, like methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, and mixtures thereof. The level of non-aqueous polar solvent is greater when more concentrated formulas are prepared. Typically, the level of non-aqueous polar solvent is from about 0% to about 40%, preferably from about 1% to about 10% and the level of water is from about 50% to about 99%, preferably from about 75% to about 95%.

The pH of the antimicrobial composition is typically from about 1.6 to about 3.0, preferably from about 2.0 to about 3.0, more preferably from about 2.0 to about 2.5. Most preferably, the pH of the antimicrobial composition is about 2.0. When the antimicrobial composition comprises citric acid as the organic acid, the pH of the composition is preferably less than about 3.0, because the first pK_a for citric acid occurs at about 3.0. At the first pK_a , the acid deprotonates and thus loses some of its antimicrobial effectiveness. The pH of the antimicrobial composition is preferably above about 2.0 because at pH below 2.0, compositions are typically required to be identified as toxic or hazardous materials.

The antimicrobial compositions of the present invention can be applied to a hard surface according to the methods described hereinbefore to achieve effective residual antimicrobial activity. In a preferred embodiment, the antimicrobial compositions are first loaded onto a substrate as described hereinafter to form a premoistened wipe product.

(B) SUBSTRATE

Referring to the components of the present invention in more detail, the premoistened wipe of the present invention includes a substrate comprising a woven or nonwoven web of natural fibers, synthetic fibers, or mixtures of natural and synthetic fibers. Suitable natural fibers include but are not limited to cellulosic fibers, such as wood pulp fibers, cotton, and rayon. Suitable synthetic fibers include fibers commonly used in textiles, including but not limited to polyester and polypropylene fibers.

Various forming methods can be used to form a suitable fibrous web for use in the present invention. For instance, the web can be made by nonwoven dry forming techniques, such as air-laying, or alternatively by wet laying, such as on a papermaking machine. Other nonwoven manufacturing techniques, including but not limited to techniques such as melt blown, spunbonded, needle punched, and hydroentanglement methods may also be used.

In one embodiment, the dry fibrous web can be an airlaid nonwoven web comprising a combination of natural fibers, staple length synthetic fibers and a latex binder. The dry fibrous web can be about 20-80 percent by weight wood pulp fibers, 10-60 percent by weight staple length polyester fibers, and about 10-25 percent by weight binder.

The dry, fibrous web can have a basis weight of between about 40 and about 90 grams per square meter. The density of the dry web can be measured after evaporating the liquid from the premoistened wipe, and the density can be less than about 0.15 grams per cubic centimeter. The density is the basis weight of the dry web divided by the thickness of the dry web, measured in consistent units, and the thickness of the dry web is measured using a circular load foot having an area of about 2 square inches and which provides a confining pressure of about 95 grams per square inch. In one embodiment, the dry web can have a basis weight of about 64 grams per square meter, a thickness of about 0.06 cm, and a density of about 0.11 grams per cubic centimeter.

In one embodiment, the dry fibrous web can comprise at least 50 percent by weight wood pulp fibers, and more preferably at least about 70 percent by weight wood pulp fibers. One particular airlaid nonwoven web which is suitable for use in the present invention comprises about 73.5 percent by weight cellulosic fibers (Southern softwood Kraft having an average fiber length

of about 2.6 mm); about 10.5 percent by weight polyester fibers having a denier of about 1.35 gram/9000 meter of fiber length and a staple length of about 0.85 inch; and about 16 percent by weight of a binder composition comprising a styrene butadiene copolymer. The binder composition can be made using a latex adhesive commercially available as Rovene 5550 (49 percent solids styrene butadiene) available from Mallard Creek Polymers of Charlotte, N.C.

One suitable airlaid nonwoven web for use in the present invention is the airlaid nonwoven web employed in PAMPERS® BABY FRESH brand baby wipes marketed by The Procter & Gamble Co. of Cincinnati, Ohio.

The pre-moistened wipe is made by wetting the dry substrate with at least 2.0 grams of liquid antimicrobial composition per gram of dry fibrous web. Preferably, the dry substrate is wetted with at least about 2.5 grams, and more preferably at least about 3.0 grams of liquid antimicrobial composition per gram of the dry fibrous web. In a preferred embodiment, the dry substrate is wetted with 3.2 grams of liquid antimicrobial per gram of dry fibrous web. A "loading factor" of 2.0 means that the dry substrate is wetted with 2.0 grams of liquid antimicrobial composition per gram of dry fibrous web.

The following patents are incorporated herein by reference for their disclosure related to webs: U.S. Patent 3,862,472 issued Jan 28, 1975; U.S. Patent 3,982,302 issued Sept. 28, 1976; U.S. Patent 4,004,323 issued Jan. 25, 1977; U.S. Patent 4,057,669 issued Nov. 8, 1977; U.S. Patent 4,097,965 issued July 4, 1978; U.S. Patent 4,176,427 issued Dec. 4, 1979; U.S. Patent 4,130,915 issued Dec. 26, 1978; U.S. Patent 4,135,024 issued Jan. 16, 1979; U.S. Patent 4,189,896 issued Feb. 26, 1980; U.S. Patent 4,207,367 issued June 10, 1980; U.S. Patent 4,296,161 issued Oct. 20, 1981; U.S. Patent 4,309,469 issued Jan 25, 1982; U.S. Patent 4,682,942 issued July 28, 1987. and U.S. Patents 4,637,859; 5,223,096; 5,240,562; 5,556,509; and 5,580,423.

In one alternative embodiment, the substrate can comprise a hydroentangled web having a basis weight of about 62 grams per square meter and comprising about 50 percent by weight rayon fibers and about 50 percent by weight polyester fibers, polypropylene fibers, or a combination thereof. In another alternative embodiment, the substrate can comprise a laminate of two outer hydroentangled webs, such as nonwoven webs of polyester fibers having a basis weight of about 30 grams per square meter, joined to an inner constraining layer, which can be in the form of net like scrim material which contracts upon heating to provide surface texture in the outer layers.

ARTICLE OF MANUFACTURE

The present article of manufacture encompasses premoistened wipe products as described hereinbefore that can be packaged in a container with a set of instructions for the consumer. The article of manufacture of the present invention typically comprises (a) container, (b) premoistened wipes, and (c) set of instructions to apply said antimicrobial composition to a hard surface and allow an effective residual antimicrobial activity amount of said antimicrobial composition on said hard surface to obtain effective residual antimicrobial activity on said surface.

Containers useful in the present article include, for example, PET tubs, flow-wrap pouches and other packaging known in the art for premoistened wipe products. Typically, premoistened wipes of the present invention are stored in the containers to reduce evaporation of the antimicrobial compositions loaded onto the premoistened wipe.

The article of manufacture of the present invention further comprises a set of instructions in association with the container. As used herein, the phrase "in association with" means the instructions are either directly printed on the container itself or presented in a different manner including, but not limited to, a brochure, print advertisement, electronic advertisement, and/or verbal communication, so as to communicate the set of instructions to a consumer of the article of manufacture.

The set of instructions typically comprise the instruction to squeeze a premoistened wipe of the present invention to release a antimicrobial composition onto a hard surface to be treated. The set of instructions can further comprise the instruction to evenly spread the antimicrobial composition across the hard surface with the substrate of the premoistened wipe. The set of instructions further comprise the instruction to allow the antimicrobial composition to remain on the treated surface, without rinsing or otherwise removing the antimicrobial composition from the treated surface. The set of instructions can further comprise the instruction to allow at least about 100 μg of organic acid, preferably citric acid, and at least about 100 μg of surfactant, preferably nonionic surfactant, per square inch of hard surface to remain on the hard surface, without rinsing or otherwise substantially removing the antimicrobial composition from the treated surface.

All patents, articles, documents, and other materials cited herein are hereby incorporated by reference, unless otherwise indicated.

The following are nonlimiting examples of the present invention.

EXAMPLE I

Effective residual antimicrobial activity of citric acid and ALFONIC® 810-6 Ethoxylated surfactant is determined according to the following protocol (Protocol No. CMB0009.TCM).

Various antimicrobial compositions consisting essentially of citric acid and ALFONIC® 810-6 Ethoxylated surfactant are applied to glass carriers and allowed to dry overnight (about 18 hours). After drying, ten microliters of a challenge organism [*Staphylococcus aureus* ATCC 6538 - (SA) or *Salmonella choleraesuis* ATCC 10708 - (SC)] are added to the treated carrier and allowed to sit for a period of time. The number of surviving organisms is then determined and the reduction of organisms is reported.

Glass carriers (3"x1") are sterilized by placing them in a dry heat sterilization oven at 180°C for 2 hours, cooled and then stored at room temperature until use.

The glass carriers are placed into sterile petri dishes (1 carrier/petri dish). Ten microliters of the antimicrobial composition is applied to each of ten carriers per challenge organism per antimicrobial composition. Using the pipette tip, the antimicrobial composition is evenly spread across a 1" x 1" surface of the carrier. The carriers are then left to dry overnight (about 18 hours) with the lids of the petri dishes left ajar.

The challenge organisms from the stock cultures are transferred into Nutrient Broth and incubated at 35°- 37°C. Daily transfers are made for at least 3 consecutive days (not to exceed 30 days). After 36-54 hours of incubation, the cultures are used to prepare inoculum. Four 48-hr tubes of the challenge organism are concentrated using centrifugation.

The inoculum is prepared using 95% culture and 5% horse serum.

The treated carriers are then inoculated with ten microliters of the inoculum and spread with the pipette tip. The numbers control count should be at least 10^4 CFU/carrier but should not exceed 10^7 CFU/carrier. The carriers are allowed to sit for the 30 minute contact time at ambient temperature. After the contact time, the carrier is transferred to twenty milliliters of Lethen Broth. The Lethen Broth containing the carriers is then vortexed. The Lethen Broth is serially diluted (1:10 dilutions) and duplicate portions of the dilutions are plated using TSA pour-plates.

All plates and all neutralizing broth tubes are incubated at 35°-37°C for 48 hours. After incubation (as appropriate), the broth culture tubes are streaked to confirm +/- growth.

The results of the foregoing testing is presented in the following chart showing the residual antimicrobial effectiveness of various antimicrobial compositions:

Micrograms of Citric Acid per sq. in. of area ¹	Micrograms of ALFONIC per sq. in. of area ²	Concentration of Citric Acid ³	Concentration of ALFONIC ⁴	Log reduction <i>Salmonella</i>	Log reduction <i>Staphylococcus</i>

750 µg	500 µg	7.5%	5.0%	6.38	6.48
750 µg	250 µg	7.5%	2.5%	6.38	4.56
375 µg	500 µg	3.75%	5.0%	6.38	3.62
375 µg	250 µg	3.75%	2.5%	6.58	5.57
275 µg	175 µg	2.75%	1.75%	5.0	5.0
175 µg	100 µg	1.75%	1.0%	1.52	3.11
35 µg	100 µg	0.35%	1.0%	0.14	0.85

¹ The micrograms quantity of citric acid applied to an one square inch of test area. After 18 hours the area is then challenged with 10 µls of test organism.

² The micrograms quantity of ALFONIC 810-6 Ethoxylated surfactant applied to an one square inch of test area. After 18 hours the area is then challenged with 10 µls of test organism.

³ The resulting concentration of citric acid produced by delivering 10 µls of microorganisms across the one sq. in. area containing a known amount of dried citric acid residual.

⁴ The resulting concentration of ALFONIC 810-6 Ethoxylated surfactant produced by delivering 10 µls of microorganisms across the one sq. in. area containing a known amount of dried ALFONIC residual.

This data demonstrates the specific amounts of organic acid (e.g., citric acid) and surfactant (e.g., a nonionic ethoxylated alcohol surfactant) required to be left on a hard surface to provide effective residual antimicrobial activity.

EXAMPLE II

The following are nonlimiting examples of antimicrobial compositions that can be utilized in the methods and articles of the present invention:

Ingredient	A	B	C	D	E	F
Organic Acid #1 ¹	1.5	1.5	2.75	1.25	1.5	0.75
Surfactant #1 ²	1.75	1.75	1.0	1.0	1.0	2.0
Solvent #1 ³	0.5	0.5	—	—	0.5	0.5
Hydrotrope ⁴	1.2	1.2	—	0.45	1.20	1.2

Suds Suppressor ⁵	—	0.0037	—	0.0030	—	—
Perfume	0.2	0.2	—	0.20	0.20	0.2
Water	Balance	Balance	Balance	Balance	Balance	Balance

¹ Citric acid commercially available from Cargill.

² Nonionic alcohol ethoxylate surfactant commercially available from Vista Chemical Company under the tradename ALFONIC® 810-6 Ethoxylated.

³ Butoxy propoxy propanol commercially available from Dow Chemical.

⁴ Sodium cumene sulfonate commercially available from Reutgers-Nease Chemical Company under the tradename NAXONATE® 45SC.

⁵ Silicone suds suppressor commercially available from Dow Corning under the tradename DOW AF.

Ingredient	G	H	I	J
Organic Acid #1 ⁶	1.5	1.5	—	—
Organic Acid #2 ⁷	—	—	4.0	—
Organic Acid #3 ⁸	—	—	—	3.0
Surfactant #1 ⁹	—	—	1.0	1.5
Surfactant #2 ¹⁰	0.4	1.0	—	—
Solvent #2 ¹¹	9.4	9.4	—	—
Solvent #3 ¹²	0.55	0.55	—	—
Solvent #4 ¹³	0.55	0.55	—	—
Perfume	0.075	0.75	—	—
Water	Balance	Balance	Balance	Balance

⁶ Citric acid commercially available from Cargill.

⁷ Acetic acid commercially available from Aldrich.

⁸ Lactic acid commercially available from Aldrich.

⁹ Nonionic alcohol ethoxylate surfactant commercially available from Vista Chemical Company under the tradename ALFONIC® 810-6 Ethoxylated.

¹⁰ Amine oxide (C₁₂) surfactant commercially available from the Stepan Company under the trade name NINOX® X9336.

¹¹ Ethanol commercially available from Aldrich.

¹² Propylene glycol t-butyl ether commercially available from Aldrich.

¹³ Di(ethylene glycol) butyl ether commercially available from Aldrich.

The antimicrobial compositions of the present invention are preferably loaded onto a substrate as described hereinbefore at a loading factor of about 3.2 to form a premoistened wipe product.

WHAT IS CLAIMED IS:

1. A method of obtaining effective residual antimicrobial activity on a hard surface comprising the steps of:
 - (a) contacting said hard surface with an effective amount of an antimicrobial composition comprising organic acid having antimicrobial action and surfactant; and
 - (b) allowing at least about 100 μg of said organic acid and at least about 100 μg of said surfactant per square inch of said hard surface to remain on said hard surface.
2. The method of Claim 1, wherein at least about 150 μg of organic acid and at least about 100 μg of surfactant per square inch of said hard surface is allowed to remain on said hard surface.
3. The method of Claim 2, wherein said organic acid is citric acid.
4. The method of Claim 3, wherein said surfactant is nonionic surfactant.
5. The method of Claim 4, wherein said nonionic surfactant is ethoxylated alcohol.
6. The method of Claim 1, wherein said method obtains effective residual antimicrobial activity on a hard surface against microbes selected from the group consisting of *Salmonella choleraesuis*, *Staphylococcus aureus*, and mixtures thereof.
7. A premoistened wipe comprising:
 - (a) a substrate; and
 - (b) an antimicrobial composition comprising:
 - (i) antimicrobially effective amount of organic acid;
 - (ii) surface tension reducing amount of surfactant;
 - (iii) optionally, suds suppressor;
 - (iv) optionally, hydrotrope;
 - (v) optionally, solvent;

(vi) optionally, perfume; and

(vii) water;

wherein said antimicrobial composition has a pH of from about 1.6 to about 3.0 and is loaded onto said substrate at a loading factor of at least about 2.0.

8. The premoistened wipe of Claim 7, wherein said organic acid is citric acid and said surfactant is nonionic surfactant.
9. The premoistened wipe of Claim 8, wherein said nonionic surfactant is ethoxylated alcohol.
10. The premoistened wipe of Claim 8, wherein suds suppressor is present at a level of from about 0.001% to about 5% by weight of said antimicrobial composition.
11. The premoistened wipe of Claim 10, wherein solvent is present at a level of from about 0.5% to about 4% by weight of said antimicrobial composition.
12. The premoistened wipe of Claim 11, wherein said solvent is n-butoxypropoxypropanol.
13. The premoistened wipe of Claim 7, wherein said substrate comprises nonwoven material.
14. A premoistened wipe comprising:
 - (a) substrate comprising nonwoven material; and
 - (b) antimicrobial composition comprising:
 - (i) from about 0.5% to about 20% by weight of said antimicrobial composition of citric acid;
 - (ii) from about 0.5% to about 15% by weight of said antimicrobial composition of nonionic surfactant;
 - (iii) optionally, suds suppressor;
 - (iv) from about 1% to about 5% by weight of said antimicrobial composition of hydrotrope;
 - (v) from about 0.5% to about 6% by weight of said antimicrobial composition of solvent;
 - (vi) optionally, perfume; and

(vii) water;

wherein said antimicrobial composition has a pH of from about 1.6 to about 3.0 and is loaded onto said substrate at a loading factor of at least about 2.0.

15. The premoistened wipe of Claim 14, wherein said nonionic surfactant is ethoxylated alcohol; said hydrotrope is sodium cumene sulfonate; and said solvent is n-butoxypropoxypropanol.

16. The premoistened wipe of Claim 15, wherein suds suppressor is present at a level of from about 0.001% to about 5% by weight of said antimicrobial composition.

17. An article of manufacture for obtaining effective residual antimicrobial activity on a hard surface comprising:

(a) container;

(b) premoistened wipe comprising:

(i) substrate; and

(ii) antimicrobial composition comprising organic acid and surfactant; wherein said antimicrobial composition has a pH of from about 1.6 to about 3.0 and is loaded onto said substrate at a loading factor of at least 2.0; and

set of instructions comprising an instruction to squeeze said premoistened wipe to release said antimicrobial composition onto said hard surface and wipe said hard

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IB 99/01101

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N25/34 A01N37/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 828 912 A (SHAFI U. HOSSAIN) 9 May 1989 (1989-05-09) * see the whole document*	1-17
X	DE 32 29 097 A (SCHÜLKE & MAYR) 9 February 1984 (1984-02-09) page 5, line 16 - page 11, line 7	1-6
X	WO 96 09761 A (DIVERSEY CORPORATION) 4 April 1996 (1996-04-04) page 2, line 13 - page 6, line 5 examples 1-5	1-6
X,P	DE 197 37 072 A (ROMAINE-NIESSNER.) 4 March 1999 (1999-03-04) column 2, line 7 - line 27 column 4, line 30 - line 38	1-6

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 21305 A (RECKITT & COLMAN) 22 May 1998 (1998-05-22) * see the whole document*	1-6
A	WO 97 46205 A (PROCTER & GAMBLE) 11 December 1997 (1997-12-11)	
A	US 4 772 501 A (JOHNSON & AL) 20 September 1988 (1988-09-20)	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Personal Application No

PCT/IB 99/01101

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4828912 A	09-05-1989	US 4975217 A	04-12-1990
		US 4897304 A	30-01-1990
		AU 554127 B	07-08-1986
		AU 8621082 A	27-01-1983
		BE 893895 A	16-11-1982
		CA 1188225 A	04-06-1985
		DE 3227126 A	03-02-1983
		DK 315482 A	21-01-1983
		FI 822542 A	21-01-1983
		FR 2509577 A	21-01-1983
		GB 2103089 A.B	16-02-1983
		GR 76879 A	04-09-1984
		JP 58135802 A	12-08-1983
		LU 84282 A	07-02-1983
		NL 8202885 A	16-02-1983
		PH 21282 A	28-09-1987
		SE 8204372 A	19-07-1982
		ZA 8204975 A	29-02-1984
DE 3229097 A	09-02-1984	CA 1244759 A	15-11-1988
		ZA 8305608 A	25-04-1984
WO 9609761 A	04-04-1996	AU 3468995 A	19-04-1996
		BR 9509103 A	14-07-1998
		CA 2198354 A	04-04-1996
		DE 69506120 D	24-12-1998
		DE 69506120 T	15-04-1999
		EP 0783245 A	16-07-1997
		ES 2124586 T	01-02-1999
		JP 10506393 T	23-06-1998
		ZA 9507952 A	18-04-1996
DE 19737072 A	04-03-1999	NONE	
WO 9821305 A	22-05-1998	GB 2319179 A	20-05-1998
		AU 4341897 A	03-06-1998
		US 5891392 A	06-04-1999
WO 9746205 A	11-12-1997	US 5830487 A	03-11-1998
		AU 3288597 A	05-01-1998
US 4772501 A	20-09-1988	US 4732797 A	22-03-1988